Study of pitch colloidal stability using a Photometric Dispersion Analyser

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SUMMARY

This paper describes the use of a photometric dispersion analyser (PDA) to study and quantify the effect of wood resin preparation and salt on the colloidal stability of wood resin dispersions. The PDA technique has two major benefits over other techniques in that it can quantify the aggregation kinetics under dynamic shear conditions and at low concentrations of colloidal material. It is very sensitive to small changes in the solution and provides information about the floc structure and homogeneity.

To ensure reproducible results when analysing colloidal wood resin dispersions, conditioning of the tubing and a constant flow rate and stirring rate were required. The PDA signal response with time for the wood resin dispersions shows three distinct regions: a growth region, a peak region, and a decay region. The slope of the initial growth region was used to measure the kinetics of coagulation and to determine the stability ratio, W. The critical coagulation concentration of different salts was also determined. The time-weighted variance of the PDA output showed that potassium salts resulted in more homogeneous aggregates than those formed with the addition of magnesium salts.

KEY WORDS

Photometric dispersion analyser, PDA, wood extractives, pitch, salt, kinetics, colloid, aggregation.

INTRODUCTION

As many paper mills worldwide reduce water consumption and close the water loop, they are faced with the need to develop strategies that reduce the accumulation of substances that cause deposits and other paper machine problems. One of the biggest problems is pitch deposition, and as salt levels increase with process water closure the problem could potentially become worse. In order to develop suitable strategies to reduce pitch deposition, a greater understanding of the effect of system closure with increasing salt levels and other components on colloidal stability and aggregation kinetics is needed.

Pitch deposits arise from the agglomeration of colloidal particles formed from the lipophilic components in the wood (*1-5*). Many factors have been found to affect the formation of deposits (*6-9*) and the behaviour of colloidal particles (*10-13*). Several studies have been undertaken investigating the effect of salt on the colloidal stability of wood extractives and have shown that salts destabilize the colloids and increase deposition tendency (*14,15*). The presence of dissolved organic material originating from the pulp has been found to stabilize the pitch colloids and reduce the effect of the salt (*5,16-18*). Work has also been undertaken to investigate the effect of synthetic polymers on pitch deposition, colloidal stability and aggregation of the wood resin colloids (*19-22*).

A number of techniques have been used to study coagulation and aggregation of colloidal particles and particle size. These include laser diffraction (*23,24*), photometric dispersion analysis (25-27), focused beam reflectance measurement (*28-31*), flow cytometry (*20,23,32,33*) and image analysis (*34-37*). Most of the techniques are based on light scattering, where the intensity of light scattered is proportional to the sixth power of the diameter for small particles.

The photometric dispersion analyser (PDA) has been found to be a useful research tool to study colloidal aggregation (*25-27*) . The PDA measures the turbidity variations of a moving colloidal suspension. The instrument measures the direct current (DC) voltage (V_{DC}), which corresponds to the average transmitted light intensity, and the root mean square (RMS) value of the fluctuations in intensity of light transmitted (V_{rms}), which indicates aggregation of the suspension. The ratio (R) of V_{rms} / V_{DC} has been shown to be a function of the particle concentration and particle size (*38*) and has been used to measure the degree of aggregation of colloidal particles. More importantly, it has been found to be unaffected by contamination of the optical surfaces or drift in the electronic components (*39*).

In this paper, a PDA has been used to study the coagulation of colloidal pitch dispersions prepared from extracted wood resins and model compounds. The effects of pitch composition and preparation along with the addition of salt on the colloidal stability and coagulation of wood resin colloidal dispersions were studied.

EXPERIMENTAL

Pulp

Thermomechanical pulp (TMP) studied was *Pinus radiata* collected from the primary refiners at Norske Skog's Boyer mill in Tasmania. The pulp was freeze dried and stored at -24°C.

Wood Resin Colloidal Dispersions

Wood resin colloidal dispersions were prepared in two ways using methods developed by both Sundberg *et al*. (*5*) and Stack *et al*. (*9*). The first, which is denoted "extracted pitch", was prepared by hexane extraction of freeze-dried TMP fibres using a soxhlet apparatus for a period of 8 hours. The hexane was removed by rotary evaporation and the resulting wood resin ("extracted pitch") was stored at -24°C until required. Prior to preparation of the aqueous pitch dispersion the extracted pitch was dissolved in acetone (99.5% purity).

The second procedure was to prepare wood resins from model compounds of abietic acid (technical grade, 70% purity, Aldrich), oleic acid (technical grade, 90% purity, Aldrich) and triolein (technical grade, 65% purity, Aldrich). Acetone

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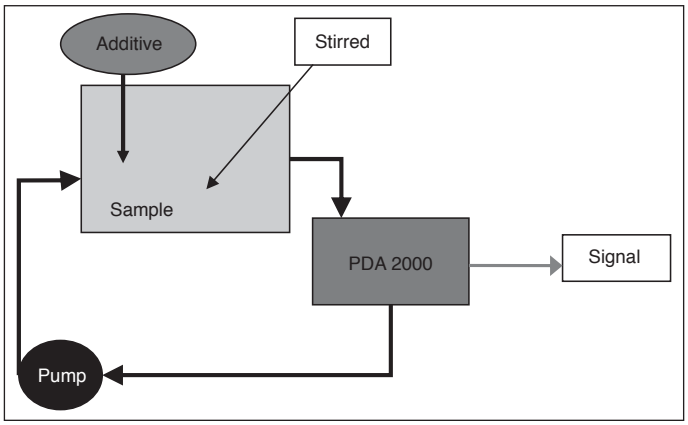

Fig. 1 Photometric dispersion analyser (PDA) experimental setup.

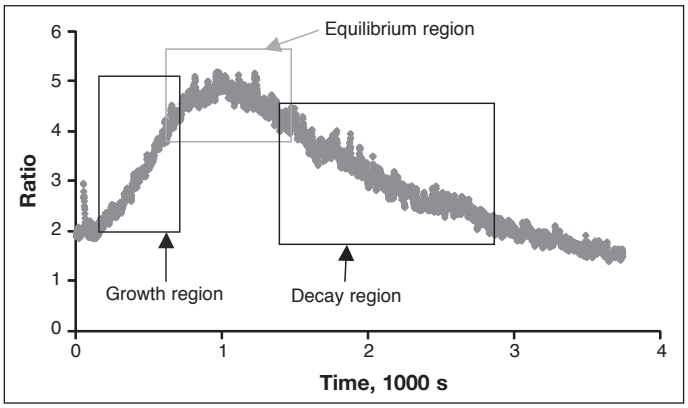

Fig. 2 PDA output (V_{rms} / V_{DC}) for undialysed hexane extracted pitch with 625 mM KCl.

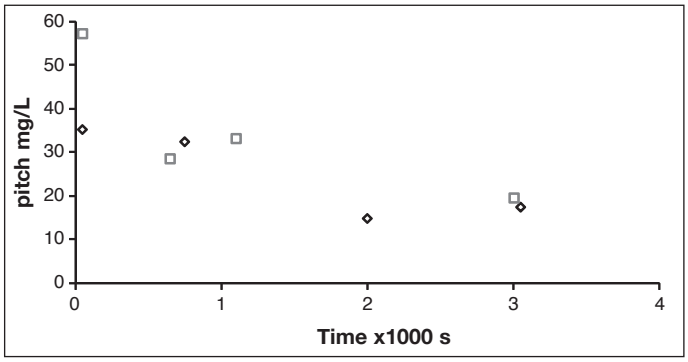

Fig. 3 Change in pitch concentration during duplicate PDA measurements of hexane extracted wood resin with 625 mM KCl.

solutions of each component were prepared as required and they were then mixed in the ratio of resin acid to fatty acid to triglycerides of 2:1:2.3. The pitch solution prepared from these model compounds was denoted "designer pitch".

Aqueous pitch dispersions were prepared by adding either acetone solutions of extracted pitch or designer pitch to a volume of distilled water with a concentration of 1 mM KNO_3, and pH adjusted to 5.5. The dispersions were dialysed for 24 hours to remove the acetone. Dialysis was conducted using a cellulose membrane tubing (Sigma D-9402, 76mm wide, >12,000 MW).

Pitch Analysis

The pitch colloids were extracted from the aqueous colloidal dispersions using tertiary-butylmethylether (*t*-BME). They were then silylated and analysed by gas chromatography (GC) as described previously (*8*).

PDA Pitch Colloid Aggregate Analysis

The PDA used in this study was a PDA 2000, from Rank Brothers, Cambridge, UK. A Cole Palmer Masterflex L/S peristaltic pump and 3 mm tubing were used to circulate the suspension. The instrument was initially calibrated with distilled water and the DC gain control was adjusted to give a DC value of 10 V as suggested in the operating manual (*31*) and also by Hopkins *et al*. (*40*). The output from the PDA is a ratio of the RMS signal to the DC voltage. A schematic of the instrument is shown in Figure 1

RESULTS AND DISCUSSION

The rate of aggregation of a colloid is dependant on a number of variables, such as concentration of colloid and electrolyte, shear, particle size, particle charge and temperature, amongst other physiochemical properties.

The addition of 625 mM KCl (at t = 0) to a colloidal dispersion prepared from extracted pitch was found to result in a change in the PDA output with time, as shown in Figure 2. The curve obtained is typical of other colloidal systems (*40*) and shows three distinct regions: an initial region with a positive slope, rising to a peak, and then tailing off. The slope of the initial growth region indicates the rate at which flocs develop/aggregate. The peak represents the steady state between aggregation and disruption of the aggregates. Most reported studies find that the ratio output maintains a constant value after the peak while some indicate that a lower steady state is reached representing the balance between floc formation and floc breakup induced by shear (*40*). In Figure 2, the graph continues to decrease to a level lower than the starting value. This could reflect a change in particle concentration or a disruption of aggregates as the weak salt induced flocs are broken down by shear to a lower equilibrium size. The time-weighted variance in the output provides an indication of the variations in the homogeneity of the colloidal flocs and can be used to measure the floc structural differences and the effect of changes in solution on the floc variation. Small variations in output signal indicate a tighter floc size distribution and a more homogeneous, dense and less porous floc structure.

During the PDA measurements shown in Figure 2, the sample concentration was also monitored by taking samples at regular time intervals. Figure 3 shows the changes in pitch concentration with time. It is noted from Figure 3 that the concentration of pitch colloids in solution was decreasing throughout the PDA experiment. This decrease in concentration is most likely due to deposition of pitch onto the tubing and/or sample vessel of the PDA apparatus.

During the initial stages of experimentation the signal response was found to increase with repeated measurements of the same solution through the apparatus. It was found that conditioning of the tubing was required prior to measurement to ensure reproducible and reliable results. It appeared that the hydrophobic tubing material and sample vessels were absorbing pitch prior to the PDA detector and a

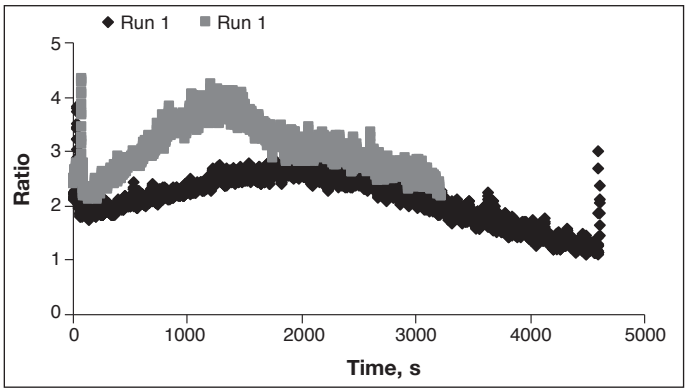

Fig. 4 Effect of conditioning of tubing on PDA output (V_{rms} / V_{DC}) for addition of 625 mM KCl to 100 mg/L extracted pitch.

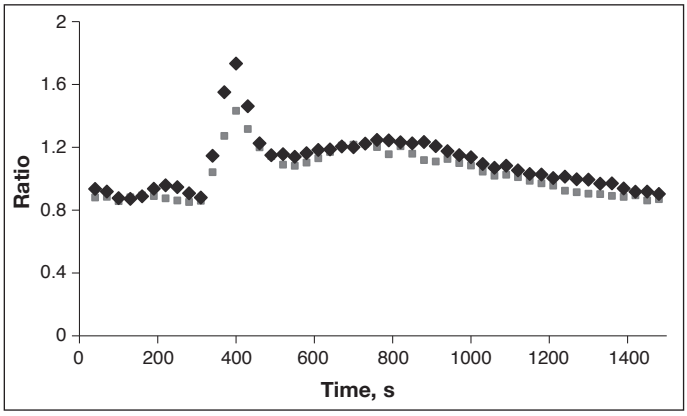

Fig. 6 PDA output (V_{rms} / V_{DC}) for duplicate measurements of dialyzed hexane extracted pitch with 600 mM KCl added.

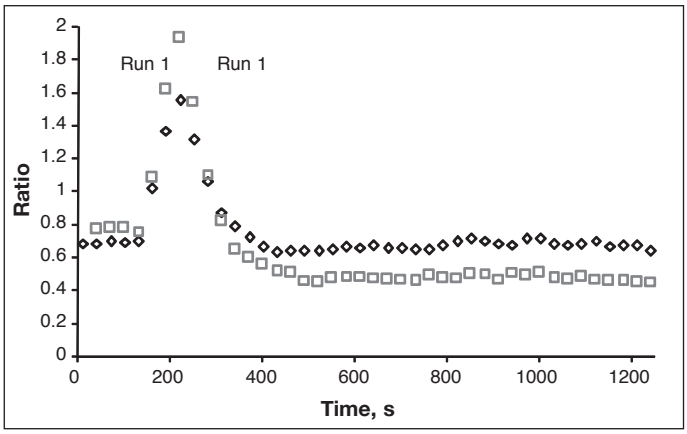

Fig. 5 PDA output (V_{rms} / V_{DC}) for duplicate measurements of deionised water after the addition of 600mM KCl.

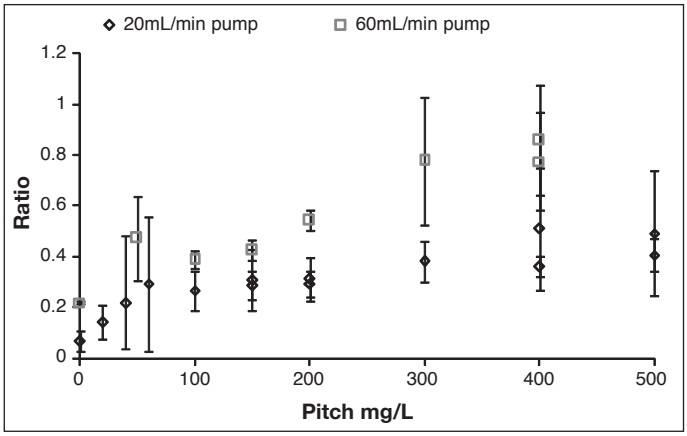

Fig. 7 Effect of pitch concentration on PDA output (V_{rms} / V_{DC}) at 20 mL/min and 60 mL/min flow rate. (Error bars are 1 standard deviation).

period of time was needed to condition these surfaces. To condition the apparatus a pitch sample was allowed to pass through the tubing for a period of 12 hours until the signal response became more reproducible. No further conditioning was required during experimentation unless changes in tubing or other components were made. Reducing the tubing length was also found to increase reproducibility and reduce the conditioning time required. Figure 4 shows the variation in the signal due to conditioning after six consecutive runs of one sample.

The PDA was found to be very sensitive to aggregation of species in solution, even at very low concentrations. The aggregation of contaminants in a deionised water sample was observed in Figure 5 on addition of 625 mM KCl to the water. The rapid return of the signal to the value of the initial baseline indicates that either only weak flocs are formed that are easily broken by shear or the particles formed reorientate and form a tighter floc structure.

It was found that the coagulation of two different colloidal materials could be followed using the PDA. Figure 6 shows the coagulation of water born contaminants and colloidal pitch. The faster coagulating material (peak at about 400 seconds) was identified as the contaminant observed in the deionised water (Fig. 5) while the slower coagulating material (broad peak at about 800 seconds) is the coagulation of colloidal extracted pitch. The difference in the peak height for the contaminant found in deionised water compared to the pitch is a result of the variation in the mobility, concentration, distribution and size of the final aggregate formed from the different coagulating substances. This capability to distinguish between different colloids is very significant. It enables the separation of coagulation of any background contaminants from the coagulation of the sample, as seen in Figure 6. Furthermore, this capacity to differentiate the coagulations of substances also makes it possible to assess if added components are being incorporated into the initial colloid or are themselves forming new colloidal material.

The reproducibility of the system is shown in both Figures 5 and 6. The signals have been smoothed with the use of a moving average over 40 points. It can be seen that there is a small variation between the replicates; however, the trends and slope for the growth region are reproducible for both samples.

During the experiments, several other factors were found to affect the behaviour of the colloid in solution and thus the PDA signal. These included the concentration, flow rate and stirring of the pitch sample. Figure 7 shows the effect of pitch concentration and flow rate (controlled by the pump speed) on the signal ouput and variance in the output. It is noted that as the concentration of pitch colloids in solution is increased, the PDA output (V_{rms} / V_{DC}) also increased. Furthermore, the increase in flow rate from 20 mL/min to 60 mL/min increased the signal output. This is thought to be the result of changes to the shear experienced by the colloid.

Within the system, it is noted that there are two sources of shear: the first is the result of pump flow rate and the second is

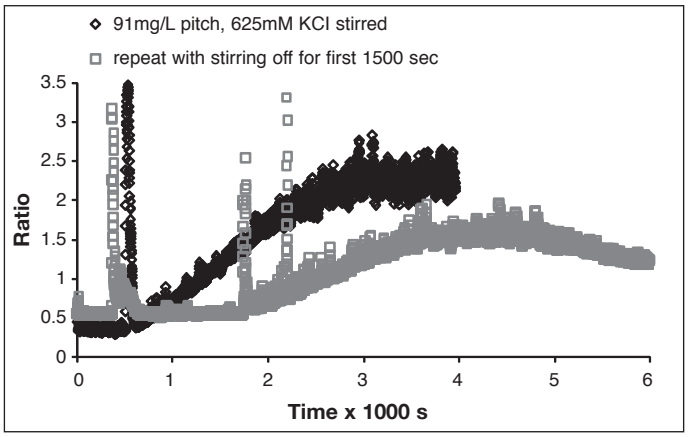

Fig. 8 Effect of stirring on PDA output (V_{rms} / V_{DC}).

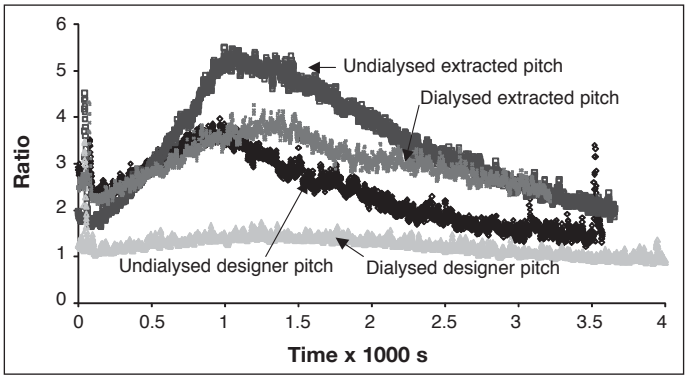

Fig. 9 Comparison of aggregation behaviour of pitch dispersions (625 mM KCl at t = 0 sec).

the result of stirring within the sample vessel. Figure 8 shows the output signal for both a stirred and an unstirred pitch sample at the same concentration of both pitch and electrolyte (625 mM KCl at t = 500 sec). The initial slope for the growth of colloids on addition of salt was greater with continuous stirring. The plot also indicates that under continuous shear conditions, the flocs reach a maximum size and then stabilise at this size, as indicated by the plateau region in Figure 8. When the experiment was repeated without stirring, the output from the PDA was unaffected.

As a result of the variability of the PDA output due to these physiochemical conditions, it was noted that the pitch concentration, sample stirring and pump flow rate are variables that must be controlled for all experiments if comparison between samples and quantification of coagulation rates are to be carried out.

The rate of aggregation for different pitch preparations of dialysed and undialysed extracted pitch and designer pitch dispersions were compared (Fig. 9). The composition of the different pitch dispersions is shown in Table 1. The results in Figure 9 show that the undialysed extracted pitch has a greater slope, and hence faster aggregation, than the dialysed extracted pitch dispersion. The same trend with dialysis was observed for designer pitch. The change in aggregation rate arising from dialysis of the sample is possibly due to the removal of acetone from solution which affects the particle size and distribution.

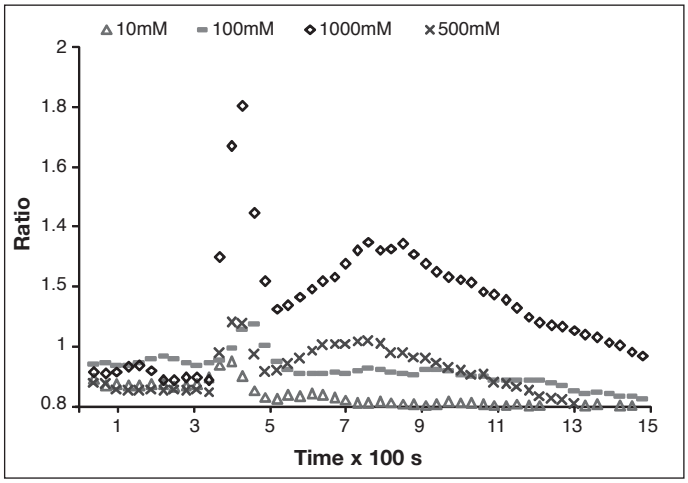

Fig. 10 Effect of KCl concentration on PDA output (V_{rms} / V_{DC}) (salt added at t=300 s).

The effects of electrolyte concentration and valency on pitch stability were quantified with the PDA to better understand the coagulation behaviour of pitch colloids within the paper mill. The effect of KCl concentration on pitch stability is illustrated in Figure 10. The initial slope, the maximum ratio level and the decay time to break up flocs were all found to increase as a function of salt concentration. The output for the PDA has been smoothed with the use of a moving average over 40 points.

The rate of pitch coagulation at the different electrolyte concentrations was quantified by the stability ratio (W) which was determined from the slopes of the curves in Figure 10 using the following equation (41):

$$W = \frac{K_1}{K^*} \qquad [1]$$

where K_1 is the fastest coagulation slope and K^* slope of coagulation due to addition of electrolyte of interest.

A plot of log W against salt concentration (Fig. 11) defines the colloidal stability of the system. At low salt additions, the system has a high value for log W and is said to be stable. As salt is added and aggregation of the colloids occurs, the system becomes unstable. The point at which log W intercepts the x-axis defines the critical coagulation concentration (CCC) for that particular salt.

The effect of salt valency on pitch stability was studied using $MgCl_2$ and KCl and the stability curves for the two salts are shown in Figure 11. The critical coagulation concentration at pH 5.5 for each salt was estimated from the curves to be CCC_{Mg2+} = 5.9 mM and CCC_{K+} = 625

Table 1
Composition of pitch dispersions

	%Fatty Acid	%Resin Acid	%Triglyceride
Extracted pitch undialysed (3% acetone)	11	48	41
Extracted pitch dialysed	11	41	48
Designer pitch undialysed (3% acetone)	19	36	45
Designer pitch dialysed	22	44	33

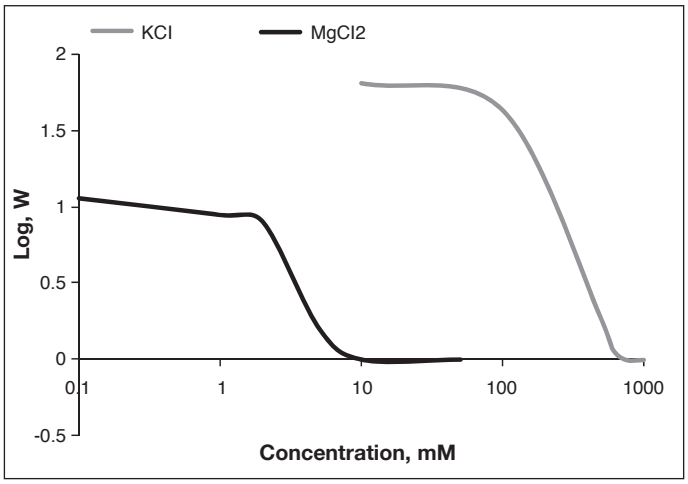

Fig. 11 Stability curves of mono and divalent salts.

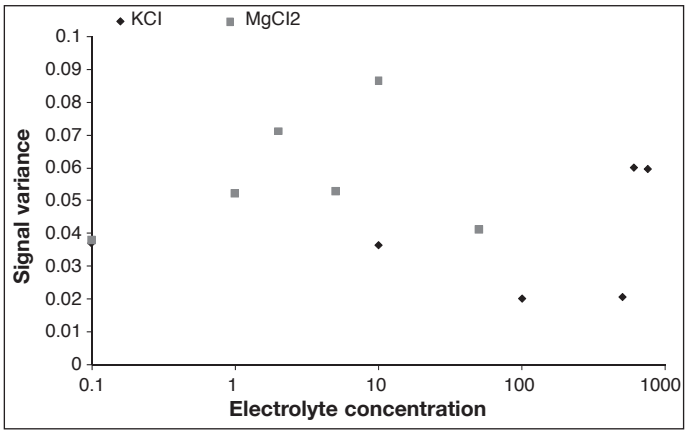

Fig. 12 Comparison of PDA output (V_{rms} / V_{DC}) variance for KCl and $MgCl_2$.

mM. These results are similar to values reported for other monovalent (Na) and divalent (Ca) salts (*5,16,17*). Swerin (42) noted that if colloidal pitch was stabilized only by electrostatic means then coagulation should occur at 100 mM NaCl and 1-2 mM $CaCl_2$. Since higher salt concentrations are needed to stabilize the pitch suspensions, it was proposed that other mechanisms (steric stabilization) might be occurring to stabilize the pitch dispersions.

Pitch colloids can be considered as "soft colloids" capable of molecular reorganization with changes to the environment. The variance in the PDA output signal is an indication of the floc homogeneity in solution as they pass the detector, with larger variance indicating increased variation in the floc size distribution The time-weighted variance in the raw ratio signal values is shown in Figure 12. It is noted that there is a higher variance in flocs following the addition of $MgCl_2$ compared to KCl. Decreases in signal variance indicate that the flocs formed when KCl is present are more uniform and tighter in structure. Above the CCC for KCl, the floc structure does appear to become less homogenous, and a greater variation in the signal is observed. The changes in variance could have two explanations: the first being that the aggregate size distribution becomes narrower, and the second explanation being that molecular reorganization and deformation of the colloids occurs.

CONCLUSIONS

Unlike other methods of investigating coagulation, the PDA is able to quantify pitch coagulation under the dynamic conditions relevant to papermaking at low concentrations. The stability ratio was determined to quantify the rate of coagulation and the critical coagulation concentrations (CCC) were found to be 5.9 mM for $MgCl_2$ and 625 mM for KCl, at 23°C and pH5.5. From the signal variation it is noted that flocs formed on addition of potassium to pitch are more homogeneous than those formed from the addition of magnesium to pitch.

Due to the sensitivity of PDA to aggregation of solution components, the technique was able to differentiate between different species that were aggregating, allowing determination as to whether or not components were aggregating as a unit or as separate entities in the solution.

In order to ensure good reproducibility when analysing pitch colloids, up to 12 hours conditioning of the tubing and sample vessel were required along with a constant flow rate through the instrument and a constant stirring rate within the sample reservoir.

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